

Soft X-ray Absorption Spectroscopy Study of Multiferroic Bi-substituted $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$

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Abstract

The electronic structures of multiferroic oxides of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($0 \leq x \leq 0.12$) have been investigated by employing photoemission spectroscopy and soft x-ray absorption spectroscopy (XAS). The measured Fe and Ti 2p XAS spectra show that Ti ions are in the Ti^{4+} states for all x and that Fe ions are Fe^{2+} - Fe^{3+} mixed-valent for $x > 0$. The valence states of Fe ions are found to be nearly trivalent for $x=0$, and decreases with increasing x from being nearly trivalent ($v(\text{Fe}) \sim 3$) for $x=0$ to $v(\text{Fe}) \sim 2.6$ for $x=0.12$. The valence states of both Ti and Ba ions do not change for all $x \leq 0.12$. Based on the obtained valence states of Fe ions, the electronic and magnetic properties of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ are explored.

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I. INTRODUCTION

Multiferroic materials exhibit the co-existence of multiple ordering, such as ferroelectricity, ferromagnetism, and ferroelasticity.[1] Multiferroic properties observed in manganese (Mn)-based oxides[2] and iron (Fe)-based oxides[3] have stimulated much research on multiferroic transition-metal oxides not only due to the potential technical application but also due to the scientific interest. As an attempt to achieve both ferroelectricity and ferromagnetism, Fe-doped $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$ has been investigated by substituting ferromagnetic Fe ions in hexagonal ferroelectric BaTiO_3 . [4–8] Room-temperature ferromagnetism has been observed in $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$ ($x < 0.1$), [4, 5] and both tetragonal and hexagonal phases exist in $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$ ceramics. The saturation magnetization and the magnetic coercivity were found to depend on the doping level as well as the fraction of the hexagonal phase in the ceramics.[6]. In $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$ system, oxygen vacancy defects and the valence states of the substituted Fe ions are expected to be important in determining the magnetic and ferroelectric properties of the system.[7] However, the reproducibility of multiferroicity and the effect of the oxygen vacancy in $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$ need be investigated more systematically.

Despite extensive studies on multiferroic transition-metal (TM) oxides, the origin of the multiferroicity has not been well understood yet. Based on the XRD (X-ray diffraction) analysis of $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$, [8] the coexistence of Fe^{3+} and Fe^{4+} ions was suggested, implying the availability of the exchange interactions among Fe^{3+} - Fe^{4+} , Fe^{3+} - Fe^{3+} , and Fe^{4+} - Fe^{4+} . Further, the Fe K -edge XANES (X-ray absorption near-edge structures) study for $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$ [9] have shown that both Fe^{3+} and Fe^{4+} ions exist in $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$, with the maximum valence states at $x \sim 0.12$. But XRD is not an element-specific experimental method that can determine the valence states of the constituent ions directly. On the other hand, Fe K -edge XANES arises mainly from the Fe $1s \rightarrow 4p$ absorption, and so Fe K -edge XANES does not directly represent the Fe $3d$ configuration in the ground state of Fe ions. Recently, the effect of the simultaneous substitutions of trivalent Bi^{3+} ions for divalent Ba^{2+} ions and trivalent Fe^{3+} (or tetravalent Fe^{4+}) ions for tetravalent Ti^{4+} ions in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{1-y}\text{Fe}_y\text{O}_3$ has been investigated.[10] Similarly as in $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$, the valence states of Fe ions are expected to play a very important role in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{1-y}\text{Fe}_y\text{O}_3$. Hence, in order to understand the origin of multiferroicity, it is crucial to determine the valence states of Fe ions directly by using element-specific experimental methods. In this aspect,

soft X-ray absorption spectroscopy (XAS) is a powerful experimental tool for studying the valence states of TM ions in solids.[11, 12]

In this work, we have investigated the electronic structures of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($0 \leq x \leq 0.12$) by employing photoemission spectroscopy (PES) and XAS. PES provides a direct observation of the occupied part of the electronic structures.[13] TM L -edge ($2p$) XAS involves the $2p \rightarrow 3d$ absorption, and so it is a very powerful experimental tool for studying the element-specific valence and spin states of TM ions in solids.[11, 12]

II. EXPERIMENTS DETAILS

Polycrystalline $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($0 \leq x \leq 0.12$) samples were synthesized by using solid-state reaction methods.[14] PES measurements were performed at the 8A1 beam line, and XAS measurements were performed at both the 8A1 and 2A beam lines of the Pohang Light Source (PLS). The base pressure of the XAS/PES chamber was better than 3×10^{-10} Torr. XAS and PES spectra were obtained at room temperature. XAS data were obtained by employing the total electron yield mode with the photon energy resolution of ~ 100 meV at $h\nu \approx 600$ eV. The overall instrumental resolution of the PES spectra was about ~ 0.4 eV at $h\nu \sim 600$ eV. All the XAS spectra were normalized to the incident photon flux.

III. RESULTS AND DISCUSSION

Figure 1 shows the survey PES spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ for $x=0.1$ and 0.12 , which are shown in the binding energy (BE) scale. These PES spectra are obtained with $h\nu \approx 630$ eV. Here we have chosen to show the samples with high Bi concentrations because they can reveal both Ba- and Bi-related peaks. All the characteristic core-level peaks of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ are observed in the measured survey PES spectra, such as O $1s$ (~ 530 eV), Ti $2p$ (~ 460 eV), Bi $4f$ (~ 160 eV), and Ba $4d$ (~ 90 eV) core levels. The large peak around ~ 290 eV is the C $1s$ core-level peak, which is often observed in polycrystalline samples. This carbon peak is likely to be due to the impurity carbons present in the grain boundaries of polycrystalline samples, which are not involved in bonding of the solids and do not affect the physical properties the samples. This figure shows that the $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ samples employed in this work are of good quality.

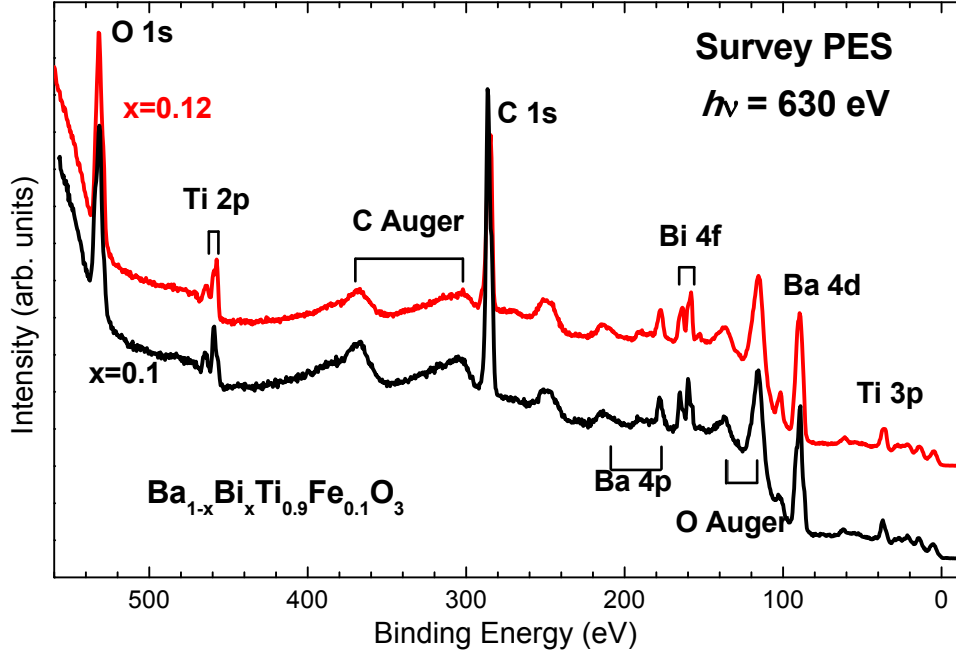


FIG. 1: (Color online) PES survey spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($x=0.1, 0.12$), obtained with $h\nu \approx 630 \text{ eV}$.

Figure 2(a) shows the measured Ti $2p$ (L -edge) XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($x=0, 0.04, 0.06, 0.1, 0.12$) in comparison to that of tetravalent (Ti^{4+}) reference oxide of TiO_2 (our data and [Ref. [15]]). The first two peaks in the low- $h\nu$ region and the other two peaks in the high- $h\nu$ region correspond to the Ti L_3 and L_2 peaks, respectively. Here L_3 and L_2 represent the spin-orbit-split $2p_{3/2}$ (L_3) and $2p_{1/2}$ (L_2) peaks, which arise from the spin-orbit coupling of the Ti $2p$ core hole. The Ti $2p$ XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ are found to be nearly identical to one another for all x , indicating that the valence states of Ti ions do not change with x . Further, they are very similar to that of TiO_2 , providing evidence that the valence states of Ti ions in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ are tetravalent (Ti^{4+}), having the $3d^0$ ground-state configuration.

Figure 2(b) shows the measured Ba $3d$ (M -edge) XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($x=0, 0.04, 0.06, 0.1, 0.12$). Here M_5 and M_4 represent the spin-orbit-split $3d_{5/2}$ and $3d_{3/2}$ peaks. This comparison shows that the Ba $3d$ XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ are nearly identical to one another for all x . This finding indicates that the valence states of Ba ions do not change with the substitution of Bi ions (x). Since the stable valence states of Ba ions are divalent, the findings of Fig. 2(b) imply that Ba ions are divalent (Ba^{2+}) in

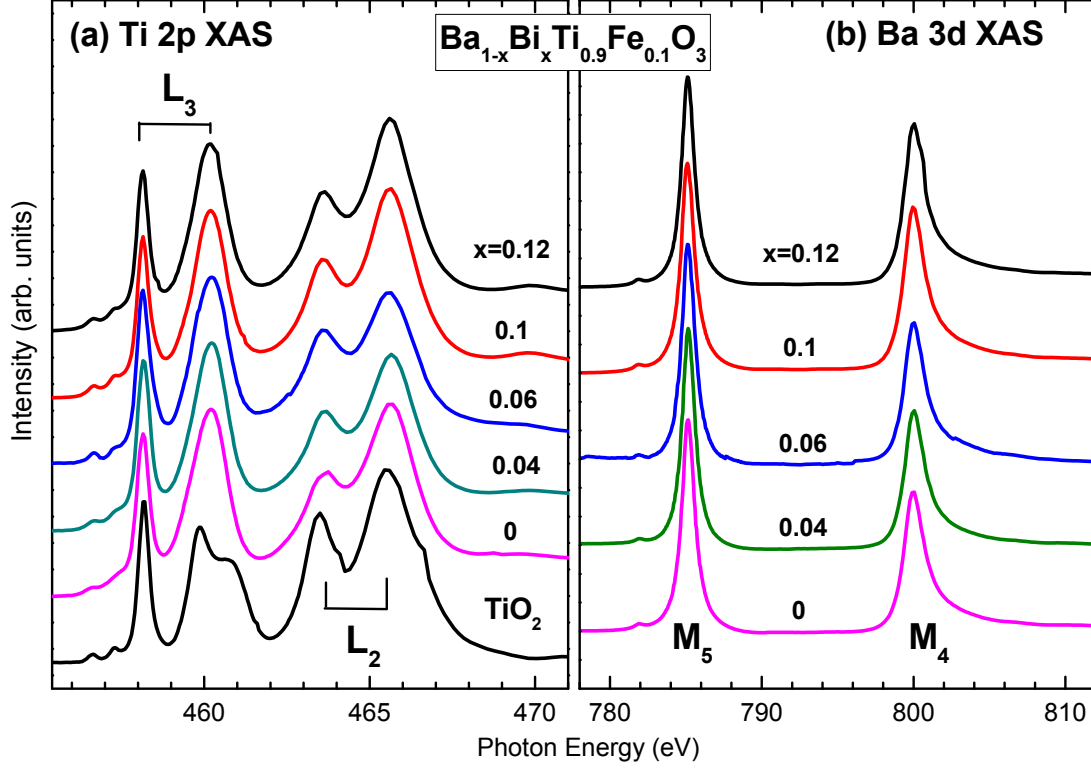


FIG. 2: (Color online) (a) Comparison of the Ti 2*p* XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ to that of TiO_2 ($0 \leq x \leq 0.12$). (b) Comparison of the Ba 3*d* XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($0 \leq x \leq 0.12$).

$\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ for $x \leq 0.12$.

We now discuss on the valence states of Fe ions in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$. Figure 3(a) shows the measured Fe 2*p* (*L*-edge) XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($0 \leq x \leq 0.12$). As a guide of the valence states of Fe ions, they are compared to those of reference Fe oxides, such as divalent (Fe^{2+}) FeO (Ref. [16, 17]), trivalent (Fe^{3+}) $\alpha\text{-Fe}_2\text{O}_3$ (Ref. [16–18]), and mixed-valent ($\text{Fe}^{2+}\text{-Fe}^{3+}$) Fe_3O_4 (Ref. [17]). Similarly as in Ti 2*p* XAS spectra, L_3 and L_2 peaks represent the spin-orbit-split L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) peaks. According to the comparison in Fig. 3(a), the line shapes of the Fe 2*p* XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ are similar to that of $\alpha\text{-Fe}_2\text{O}_3$ (Fe^{3+}) but quite different from that of FeO (Fe^{2+}). This observation indicates that Fe ions in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ are close to being trivalent (Fe^{3+}),

On the other hand, the intensities of the low- $h\nu$ peak (peak "A") with respect to that of the high- $h\nu$ peak (peak "B") in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ are slightly different from that of $\alpha\text{-Fe}_2\text{O}_3$. Further, $I(A)/I(B)$ (=the relative intensity of peak "A" to that of peak "B") changes

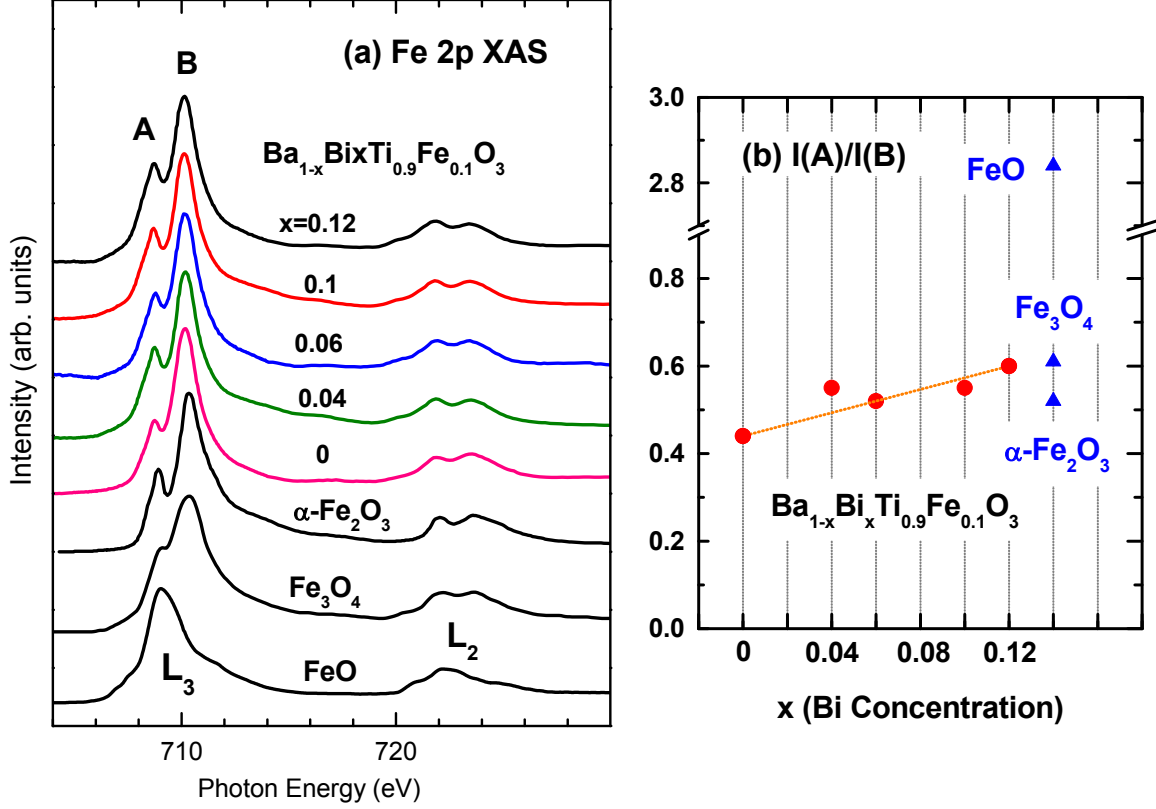


FIG. 3: (Color online) (a) The Fe 2p XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($0 \leq x \leq 0.12$) in comparison with those of reference Fe oxides of trivalent (Fe^{3+}) $\alpha\text{-Fe}_2\text{O}_3$, divalent (Fe^{2+}) FeO , and mixed-valent ($\text{Fe}^{2+}\text{-Fe}^{3+}$) Fe_3O_4 . (b) Plot of the intensity ratio of Fe L_3 XAS spectra of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ and reference Fe oxides.

slightly for different x values, which is shown better in the relative intensity ratio of $I(A)/I(B)$ in Fig. 3(b). In order to interpret the meaning of $I(A)/I(B)$ values in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$, we examine the lineshapes and $I(A)/I(B)$ of reference Fe oxides. Note that, in divalent (Fe^{2+}) FeO , the peak "A" is dominant and the peak "B" appears as a high- $h\nu$ shoulder. $I(A)/I(B)$ increases from trivalent (Fe^{3+}) $\alpha\text{-Fe}_2\text{O}_3$ (0.52) to mixed-valent ($\text{Fe}^{2+}\text{-Fe}^{3+}$) Fe_3O_4 (0.63) and divalent (Fe^{2+}) FeO (> 1). This trend is shown more clearly in Fig. 3(b).

Figure 3(b) shows that $I(A)/I(B)$ in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ increases slightly with increasing x . $I(A)/I(B)$ for $x=0$ is lower than that of $\alpha\text{-Fe}_2\text{O}_3$, but $I(A)/I(B)$ for $x=0.12$ is similar to that of Fe_3O_4 . Such a trend in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ and the relative magnitudes with the reference Fe oxides indicate that, in $x=0$ ($\text{BaTi}_{0.9}\text{Fe}_{0.1}\text{O}_3$), Fe ions are nearly trivalent (Fe^{3+}), and that, with the substitution of Bi ions for Ba ions ($x > 0$), the Fe^{2+} component appears, resulting in $\text{Fe}^{2+}\text{-Fe}^{3+}$ mixed-valent states. For $x=0.12$ ($\text{Ba}_{0.88}\text{Bi}_{0.12}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$),

the valence states of Fe ions become similar to that of Fe_3O_4 ($v(\text{Fe}) \sim 2.67$). This finding is consistent with the expected trend since Bi ions are generally trivalent (Bi^{3+}) whereas Ba ions are divalent (Ba^{2+}), as confirmed by the measured Ba 3d XAS spectra (see Fig. 2(b)). Considering the charge neutrality conditions in insulating oxides, the substitution of trivalent Bi^{3+} ions for divalent Ba^{2+} ions would cause the decreasing valence states of Fe ions.

Our Fe 2p, Ti 2p, and Ba 3d XAS study on $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ shows that Ti ions are tetravalent (Ti^{4+}) and Ba ions are divalent (Ba^{2+}) for all x in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($x \leq 0.12$). In contrast, with increasing x , the valence states of Fe ions decrease from being nearly trivalent ($v(\text{Fe}) \sim 3$) for $x=0$ (no Bi ions) to being mixed-valent for $x > 0$ (Fe^{2+} - Fe^{3+} mixed-valent) and to become $v(\text{Fe}) \sim 2.6$ for $x=0.12$. This finding refutes the suggestion of the Fe^{3+} - Fe^{4+} mixed-valence states in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$. Hence the idea of the exchange interactions among Fe^{3+} - Fe^{4+} , Fe^{3+} - Fe^{3+} , and Fe^{4+} - Fe^{4+} , need be examined more carefully. This work suggests that the valence states of Fe ions play an important role in determining the electronic and magnetic properties of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$.

IV. CONCLUSIONS

The electronic structures of of multiferroic oxides of $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($0 \leq x \leq 0.12$). have been investigated by employing synchrotron-radiation excited PES and XAS. Via Fe and Ti 2p XAS measurements, the valence states of Fe and Ti ions have been determined experimentally. The valence states of Fe ions are found to be Fe^{2+} - Fe^{3+} mixed-valent for $x > 0$ but nearly trivalent for $x=0$. The valence states of Fe ions are found to decreases from being nearly trivalent for $x=0$ ($v(\text{Fe}) \sim 3$) to $v(\text{Fe}) \sim 2.6$ for $x=0.12$. The valence states of Ti ions do not change with x for $x \leq 0.12$, and stay being tetravalent (Ti^{4+}). The valence states of Ba ions are close to being divalent (Ba^{2+}) and remain unchanged for $x \leq 0.12$. The decreasing trend of valence states of Fe ions in $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ with x will play an important role in the electronic and magnetic properties of this system.

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